

DECLARATION

I, Antonella DE GREGORI of Via Borgonuovo 10, MILAN, Italy declare:

1. that I am well acquainted with the Italian and English languages;
2. that I am a sworn translator from and into the Italian and English languages;
3. that the translation contained therewith has been prepared by me and is a true translation from the Italian language of the document issued by the Italian Ministry of Industry, Trade and Handicraft - Italian Patent and Trademark Office - certifying the filing on the

31th day of JULY 2002 under No. MI2002A001711

by POLIMERI EUROPA S.p.A.

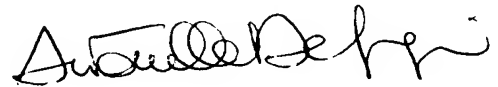
of an application for grant of a patent for industrial invention having the following title:

"BEADS OF EXPANDABLE VINYLAROMATIC POLYMERS AND PROCESS FOR THEIR PREPARATION"

and of the specification and filing certificate attached thereto.

And I make this declaration conscientiously believing the same to be true.

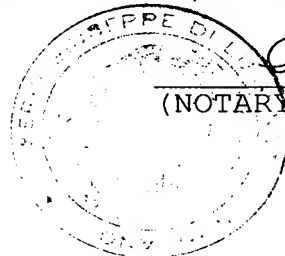
Milan, Italy
this 14th day of January 2008.



(Antonella DE GREGORI)

Declared before me, in the city of Milan, Italy, by the aforesaid Antonella DE GREGORI

this 15th day of January 2008 day of January 2008




(NOTARY PUBLIC)

TO THE MINISTRY OF INDUSTRY, TRADE AND HANDICRAFT FORM A
Central Patent Office ROME
APPLICATION FOR PATENT FOR INDUSTRIAL INVENTION, LATE FILING OF
DOCUMENTS, ANTICIPATED LAYING-OPEN TO PUBLIC INSPECTION

A. APPLICANT(S):

1) Name *POLIMERI EUROPA S.p.A.*
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B. APPLICANT REPRESENTATIVE C/O I.T.P.O.

Surname, Name *CAVALIERE Giambattista et al.* Fiscal Code
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C.ELECTED DOMICILE ADDRESSEE see above
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D.TITLE Proposed Classification *C08J* sub-group
"BEADS OF EXPANDABLE VINYLAROMATIC POLYMERS AND PROCESS FOR
THEIR PREPARATION"
ANTICIPATED LAYING-OPEN TO THE PUBLIC: Y/N PETITION RECORD

E. DESIGNATED INVENTORS:

Surname, Name	Surname, Name
1) <i>LANFREDI Roberto</i>	3)
2) <i>GHIDONI Dario</i>	4)

F. PRIORITY:

State Type no. date Encl. Y/N POSTPONED FILING DATE RECORD

1) none
2)

G. COLLECTING CENTRE OF MICROORGANISM CULTURES, STYLE

H. SPECIAL NOTES:

DOCUMENTS ENCLOSED:

CANCELLATION OF POSTPONED
FILING DATE RECORD no.
TO BE COMPARED WITH EACH
PRIORITY

Doc.1)	2PROV. no. 17 pages	abstract with drawing, description and claims (1 copy compulsory)
Doc.2)	0 PROV. no.00 tables	drawing (1 copy compulsory if mentioned in the description)
Doc.3)	0 TO FOLLOW	Power of Attorney
Doc.4)	1 TO FOLLOW	Inventor's Designation
Doc.5)	TO FOLLOW	Priority Docs. with Italian translation
Doc.6)	TO FOLLOW	Authorisation or Assignment Deed
Doc.7)	TO FOLLOW	Full Applicant's name
8)	Certification of payment	for EURO 188,51= compulsory

FILLED IN ON

Signature of Applicant(s) THE AGENT Ing. Giambattista CAVALIERE

TO BE CONTINUED XXX/NO

CERTIFIED COPY HEREOF IS REQUESTED YES/XX

PROVINCIAL OFFICE INDUSTRY, TRADE AND HANDICRAFT OF MILANO

Code:15

FILING CERTIFICATE. Application number MI2002A001711 Reg.A

In the year TWOTHOUSANDANDTWO on the 31th day of the month of A
JULY

The above mentioned Applicant(s) has (have) filed before me the
undersigned the present application consisting of no. 01
additional sheets for the grant of the patent aforementioned.

I. VARIOUS NOTES BY THE ATTESTING OFFICER:

For the Applicant signature

ATTESTING OFFICER signature

ABSTRACT OF THE INVENTION WITH FORMAL DRAWING DESCRIPTION AND CLAIM

APPLICATION NUMBER MI2002A001711 FILING DATE 31.07.2002

PATENT NUMBER

ISSUE DATE

D. TITLE: "BEADS OF EXPANDABLE VINYLAROMATIC POLYMERS AND
PROCESS FOR THEIR PREPARATION"

L. ABSTRACT

- 10 Beads of expandable vinylaromatic polymers which comprise:
- a) a matrix obtained by polymerizing 50-100% by weight of one or more vinylaromatic monomers and 0-50% by weight of at least one copolymerizable monomer;
 - b) 1-10% by weight, calculated with respect to the polymer
 - 15 (a), of an expanding agent englobed in the polymeric matrix;
 - c) 2 ppm-2% by weight, calculated with respect to the polymer (a), of an anti-lumping additive, distributed on the surface of the beads, comprising oxides of metals of groups
 - 20 IB, IIB and VIIIB.

M. DRAWING

"BEADS OF EXPANDABLE VINYLAROMATIC POLYMERS AND PROCESS FOR THEIR PREPARATION"

in the name of POLIMERI EUROPA S.p.A.

with head office in BRINDISI, Via Enrico Fermi 4

The present invention relates to beads of expandable
10 vinylaromatic polymers and a process for their preparation.

More specifically, the present invention relates to an expandable polystyrene in the form of beads with a reduced formation of lumps and the process for its preparation.

Vynylaromatic polymers, and among these, polystyrene
15 in particular, are known products which have been adopted for a long time for preparing compact and/or expanded articles which can be used in various applicative sectors, among which the most important are household appliances, the transport and building industries, office machines,
20 etc. A particularly interesting sector is the field of thermal insulation, where vinylaromatic polymers are essentially used in expanded form.

These expanded products are obtained by swelling, in a pre-expander, beads of expandable polymer previously im-
25 pregnated with an expanding agent and molding the swollen

particles inside a closed mould by means of the contemporaneous effect of pressure and temperature.

The swelling, or pre-expansion, of the particles is generally effected with vapour, or another gas, maintained at a temperature slightly higher than the glass transition temperature (T_g) of the polymer. During this phase, the particles tend to stick to each other and to avoid this drawback, they are treated with additives generally known as anti-lumping additives.

The addition of metallic stearates, such as magnesium stearate, is known, for example. This additive is extremely effective in preventing the beads from sticking during the pre-expansion phase but results in poor adhesion in the moulding phase during the preparation of the end-products.

U.S. patent 3,520,833 describes the use of lecithin, added with the expanding agent during the impregnation of the particles, as anti-lumping additive. Unfortunately, lecithin gives the end-products an unacceptable odour making their use problematical.

U.S. patent 3,444,104 describes the use of calcium and silicon aluminates. The lumps, in this case, are eliminated and the adhesion remains acceptable. The density of the beads in expansion, however, is poor.

U.S. patent 3,462,293 describes the use of a polymeric latex, for example polyethylene or SAN copolymer, deposited

on the particles. The subsequent drying treatment of the latex with air, however, requires long times which make the preparation process quite unsuitable for industrial development.

5 Finally, European patent 449,065 describes the use of oxides such as silica, alumina and titanium oxide. Although these products have a good capacity against the formation of lumps, they have the disadvantage, as specified above, of reducing the adhesion of the expanded beads during the
10 moulding phase.

 There are evident disadvantages associated with these systems for avoiding the formation of lumps as they either jeopardize the adhesion of the expanded beads, or the expansion of the beads themselves or they require processes,
15 for example drying, which are too elaborate for being conveniently used in the industrial field.

 The Applicant has now found a simple system for eliminating the formation of agglomerates of swollen vinylaromatic polymer beads without jeopardizing the subsequent ad-
20 hesion and/or expandability.

 An object of the present invention therefore relates to beads of expandable vinylaromatic polymers which comprise:

 a) a matrix obtained by polymerizing 50-100% by weight of
25 one or more vinylaromatic monomers and 0-50% by weight of

at least one copolymerizable monomer;

b) 1-10% by weight, calculated with respect to the polymer (a), of an expanding agent englobed in the polymeric matrix;

5 c) 2 ppm-2% by weight, calculated with respect to the polymer (a), of an anti-lumping additive, distributed on the surface of the beads, selected from oxides of metals of groups IB and VIIIB or from mixtures consisting of oxides of metals of groups IB, IIB and VIIIB and esters of C₈-C₂₅
10 fatty acids with the same metals.

A further object of the present invention relates to a process for the preparation of expandable vinylaromatic polymer beads which comprises:

- polymerizing 50-100% by weight of one or more vinylaromatic monomers and 0-50% by weight of at least one copolymerizable monomer;
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- englobing an expanding agent in the polymeric matrix; and
- distributing on the surface of the beads obtained 2 ppm-
20 2% by weight, calculated with respect to the polymer, of an anti-lumping additive selected from oxides of metals of groups IB and VIIIB or from mixtures consisting of oxides of metals of groups IB, IIB and VIIIB and esters of C₈-C₂₅ fatty acids with the same metals.

25 According to the present invention, the vinylaromatic

polymers can be obtained with a polymerization process in aqueous suspension or continuous mass. In particular, the polymerization in suspension of the vinylaromatic monomer is carried out under conditions and in the presence of additives well known in the art. In addition to the suspending agent, selected from insoluble inorganic salts, for example calcium or magnesium such as tricalcium phosphate or magnesium phosphate, or from organic suspending agents such as polyvinylpyrrolidone, the polymerization is carried out in the presence of an initiating system or an expanding system.

The initiating system generally comprises two peroxides, one with a halving time of an hour at 85-95°C and the other with a halving time of an hour at 110-120°C. Examples of these initiators are benzoylperoxide and terbutylperbenzoate.

Any expanding agent capable of being englobed in the polymeric matrix can be used in a combination with the vinylaromatic polymers object of the present invention. In general, liquid substances are used, with a boiling point ranging from 10 to 100°C, preferably from 20 to 80°C. Typical examples are aliphatic hydrocarbons, freon, carbon dioxide, water, etc.

The expanding agent can be added to the polymer during the polymerization phase in suspension, or, alternatively,

by impregnation of the beads produced at the end of the polymerization or by injection into the molten polymer according to the continuous mass preparation process. At the end of the addition, a polymer is obtained in the form of beads, which can be transformed to produce expanded articles with a density ranging from 5 to 50 g/l, preferably from 8 to 25 g/l, with an excellent thermal insulation capacity. In order to favour the retention of the expanding agent in the polymeric matrix, additives capable of forming bonds both of the weak type (for example hydrogen bridges) or strong type (for example acid-base adducts), can be used with the expanding agent. Examples of these additives are methyl alcohol, isopropyl alcohol, dioctylphthalate, dimethylcarbonate, compounds containing an amine group, etc. These additives are generally added during the polymerization and/or englobed in the polymer together with the expanding agent.

The expanding agents are preferably added during the polymerization phase and are selected from aliphatic or cycloaliphatic hydrocarbons containing from 3 to 6 carbon atoms, such as n-pentane, iso-pentane, cyclopentane or their mixtures; halogenated derivatives of aliphatic hydrocarbons containing from 1 to 3 carbon atoms such as, for example, dichlorodifluoromethane, 1,2,2-trifluoroethane, 1,1,2-trifluoroethane; carbon dioxide and water.

The term "vinylaromatic monomer", as used in the present description and claims, essentially refers to a product which corresponds to the following general formula:

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wherein n is zero or an integer ranging from 1 to 5, R is a hydrogen atom or a methyl and Y is a halogen, such as chlorine or bromine, or an alkyl or alkoxyl radical having from
10 1 to 4 carbon atoms.

Examples of vinylaromatic monomers having the general formula defined above are: styrene, α -methylstyrene, methylstyrene, ethylstyrene, butylstyrene, dimethylstyrene,
15 mono-, di-, tri-, tetra- and penta-chlorostyrene, bromostyrene, methoxy-styrene, acetoxy-styrene, etc. Styrene and α -methylstyrene are the preferred vinylaromatic monomers.

The vinylaromatic monomers having general formula (I) can be used alone or in a mixture of up to 50% by weight
20 with other copolymerizable monomers. Examples of these monomers are (meth)acrylic acid, C_1 - C_4 alkyl esters of (meth)acrylic acid, such as methyl acrylate, methylmethacrylate, ethyl acrylate, ethylmethacrylate, isopropyl acrylate, butyl acrylate, amides and nitriles of
25 (meth)acrylic acid such as acrylamide, methacrylamide,

acrylonitrile, methacrylonitrile, butadiene, ethylene, divinylbenzene, maleic anhydride, etc. Preferred copolymerizable monomers are acrylonitrile and methylmethacrylate.

The vinylaromatic polymer or copolymer which is obtained has a molecular weight Mw ranging from 50,000 to 250,000, preferably from 70,000 to 200,000. In general, greater details on a process for the preparation of expandable vinylaromatic polymers in aqueous solution or, more generally, on polymerization in suspension, can be found in Journal of Macromolecular Science, Review in Macromolecular Chemistry and Physics c31 (263) 215-299 (1991) or in international patent application WO 98/51734.

Conventional additives, generally used with commercial materials, such as pigments, stabilizers, flame-retardant agents, antistatic agents, detaching agents, shock-resistant agents, etc., can be added to the expandable vinylaromatic polymers obtained with the process, object of the present invention. In particular, it is preferable to add mineral fillers of athermanous materials during the polymerization, such as graphite or refracting agents such as titanium dioxide, in a quantity ranging from 0.05 to 25% by weight, calculated with respect to the resulting polymer.

At the end of the polymerization, substantially spherical polymer beads are obtained, with an average diameter ranging from 0.2 to 2 mm, inside which the expanding

agent is homogeneously dispersed.

To improve the stability of the suspension, it is possible to increase the viscosity of the reagent solution by dissolving the vinylaromatic polymer therein, in a concentration ranging from 1 to 30% by weight, preferably from 5 to 20%, calculated with respect to the monomer alone. The solution can be obtained either by dissolving a preformed polymer (for example fresh polymer or the waste products of previous polymerizations and/or expansions) in the reagent mixture or by pre-polymerizing the monomer, or mixture of monomers, in mass, in order to obtain the above concentrations, and then continuing the polymerization in aqueous suspension in the presence of the remaining additives.

At the end of the polymerization, the beads are discharged from the polymerization reactor, washed and dried.

The beads produced are subjected to pre-treatment generally applied to traditional materials and which essentially consists in:

1. coating the beads with a liquid antistatic agent such as amines, tertiary alkylamines, ethylene oxide-propylene oxide copolymers, etc. The purpose of this agent is to facilitate both the adhesion of the coating and also the screening of the beads prepared in suspension;
2. applying the coating to the above beads, said coating essentially consisting of a mixture of mono-, di- and

tri-esters of glycerin (or other alcohols) with fatty acids; and

3. distributing on the surface of the beads, the anti-lumping additive preferably selected from powders of oxides of iron (Fe_2O_3), copper (CuO) and zinc (ZnO), optionally mixed with the corresponding ester of fatty acids such as stearic acid, palmitic acid, myristic acid, etc. The anti-lumping additive is generally used in the form of powders with an average particle-size ranging from 0.1 to 50 μm .

Some illustrative but non-limiting examples are provided for a better understanding of the present invention and for its embodiment.

COMPARATIVE EXAMPLE 1

100 parts of styrene monomer, 0.30 parts of benzoyl peroxide, 0.15 parts of terbutylperbenzoate, 100 parts of demineralized water, 0.2 parts of tricalcium phosphate and 20 ppm of sodium dodecylbenzenesulfonate, were charged into a 2 litre reactor equipped with a stirrer.

The mixture was then heated to 90°C for 4 hours and to 125°C for a further 6 hours.

The expanding agent (7 parts of n-pentane) was added during the rise from 90 to 125°C.

At the end of the polymerization, the beads were centrifuged, washed with water and dried with air at room tem-

perature.

0.02% of diethanol alkyl amine was added to the beads of expandable polymer thus produced, which were then sieved, separating the fraction with a diameter ranging
5 from 0.4 to 0.6 mm.

0.25% of glycerylmonostearate and 0.1% of magnesium stearate were then added to the fraction.

The product is pre-expanded the following day with vapour at a temperature of 100°C at a density of 20 g/l, evaluating the quantity of clots, which proved to be practically zero.
10

The expanded beads are then aged for a day and used the following day for the moulding of boxes (thickness 20 mm) at a pressure of 0.5 bars. The adhesion of the beads
15 proved to be 5%.

COMPARATIVE EXAMPLE 2

The beads polymerized according to Comparative example 1 were lubricated with 0.02% of diethanol alkyl amine and sieved, separating the fraction with a diameter ranging
20 from 0.4 to 0.6 mm.

0.25% of glycerylmonostearate and 0.1% of zinc stearate were then added to the fraction.

The product is pre-expanded the following day with vapour at a temperature of 100°C at a density of 20 g/l, evaluating the quantity of lumps, which proved to be equal
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to 3%.

The expanded beads are then aged for a day and used the following day for the moulding of boxes (thickness 20 mm) at a pressure of 0.5 bars. The adhesion of the beads proved to be 40%.

COMPARATIVE EXAMPLE 3

The beads polymerized according to Comparative example 1 were lubricated with 0.02% of diethanol alkyl amine and sieved, separating the fraction with a diameter ranging from 0.4 to 0.6 mm.

0.25% of glycerylmonostearate and 0.1% of silica Sipernat D 17 (diameter of 10 μ m) of Degussa, were then added to the fraction.

The product is pre-expanded the following day with vapour at a temperature of 100°C at a density of 20 g/l, evaluating the quantity of lumps, which proved to be absent.

The expanded beads are then aged for a day and used the following day for the moulding of boxes (thickness 20 mm) at a pressure of 0.5 bars. The adhesion of the beads proved to be 5%.

COMPARATIVE EXAMPLE 4

The beads polymerized according to Comparative example 1 were lubricated with 0.02% of diethanol alkyl amine and sieved, separating the fraction with a diameter ranging

from 0.4 to 0.6 mm.

0.25% of glycerylmonostearate and 0.1% of alumina, with a diameter $<10\text{ }\mu\text{m}$, commercialized by Aldrich, were then added to the fraction.

5 The product is pre-expanded the following day with vapour at a temperature of 100°C at a density of 20 g/l , evaluating the quantity of lumps, which proved to be absent.

10 The expanded beads are then aged for a day and used the following day for the moulding of boxes (thickness 20 mm) at a pressure of 0.5 bars . The adhesion of the beads proved to be 5% .

EXAMPLE 1

15 Comparative example 2 is repeated, reducing the zinc stearate to 0.05% and adding 0.05% of zinc oxide. There were no lumps and the adhesion was excellent, equal to 70% .

EXAMPLE 2

20 Comparative example 1 is repeated, substituting the magnesium stearate with 5 ppm of ferric oxide in powder form, produced by Aldrich, with an average particle diameter of about $1\text{ }\mu\text{m}$. There were no lumps and the adhesion was excellent, equal to 80% .

EXAMPLE 3

25 Comparative example 1 is repeated, substituting the magnesium stearate with 5 ppm of copper oxide (CuO) in pow-

der form, produced by Aldrich, with an average particle diameter $< 5 \mu\text{m}$. There were no lumps and the adhesion was excellent, equal to 70%.

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CLAIMS

1. Beads of expandable vinylaromatic polymers which comprise:

- a) a matrix obtained by polymerizing 50-100% by weight of
5 one or more vinylaromatic monomers and 0-50% by weight of
at least one copolymerizable monomer;
- b) 1-10% by weight, calculated with respect to the polymer
(a), of an expanding agent englobed in the polymeric matrix;
- 10 c) 2 ppm-2% by weight, calculated with respect to the polymer
(a), of an anti-lumping additive, distributed on the
surface of the beads, selected from oxides of metals of
groups IB and VIIIB or from mixtures consisting of oxides
of metals of groups IB, IIB and VIIIB and esters of C₈-C₂₅
15 fatty acids with the same metals.

2. The beads of expandable vinylaromatic polymers according to claim 1, having an average molecular weight Mw ranging from 50,000 to 250,000.

3. The beads of expandable vinylaromatic polymers according to claim 1 or 2, wherein the beads are substantially
20 spherical with an average diameter ranging from 0.2 to 2
mm.

4. A process for the preparation of beads of expandable vinylaromatic polymers which comprises:

- 25 - polymerizing 50-100% by weight of one or more vinylaro-

matic monomers and 0-50% by weight of at least one copolymerizable monomer;

- englobing an expanding agent in the polymeric matrix;
and

5 - distributing on the surface of the beads obtained 2 ppm-
2% by weight, calculated with respect to the polymer, of
an anti-lumping additive selected from oxides of metals
of groups IB and VIIIB or from mixtures consisting of
oxides of metals of groups IB, IIB and VIIIB and esters
10 of C₈-C₂₅ fatty acids with the same metals.

5. The process according to claim 4, wherein the polymerization is carried out in aqueous suspension or in continuous mass.

6. The process according to claim 4 or 5, wherein the polymerization is carried out in suspension in the presence
15 of a suspending agent, an initiating system and an expanding system.

7. The process according to claim 6, wherein the expanding system consists of liquid substances with a boiling
20 point ranging from 10 to 100°C.

8. The process according to any of the previous claims from 4 to 7, which comprises:

1. coating the beads with a liquid antistatic agent such as
amines, tertiary alkylamines, ethylene oxide-propylene
25 oxide copolymers;

2. applying the coating to the above beads, said coating essentially consisting of a mixture of mono-, di- and tri-esters of glycerin (or other alcohols) with fatty acids; and

5 3. distributing on the surface of the beads, the anti-lumping additive preferably selected from powders of oxides of iron (Fe_2O_3), copper (CuO) and zinc (ZnO), optionally mixed with the corresponding ester of fatty acids.

10 9. The process according to any of the claims from 4 to 8, wherein the anti-lumping additive is used in the form of powders with an average particle-size ranging from 0.1 to 50 μm .

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